Inorganic chemistry

Lecturer . 9

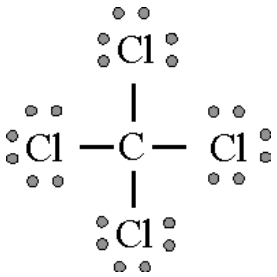
Molecular Geometry and Bonding Theories

Molecular Geometries

Molecular shapes, or geometries, are critical to molecular recognition and function.

Molecular Geometries

The Lewis structure of carbon tetrachloride:



- **Provides information about connectivities**
- **Provides information about valence orbitals**
- **Provides information about bond character**

However, the Lewis structure provides no information about the shape of the molecule

Exceptions to the Octet Rule

- ***There are three general ways in which the octet rule breaks down:***
  1- **Molecules with an odd number of electrons**
  2- **Molecules in which an atom has less than an octet**
  3- **Molecules in which an atom has more than an octet**

- ***Also, Expanded valence shells are observed only for elements in period 3 (i.e. n=3) and beyond.***

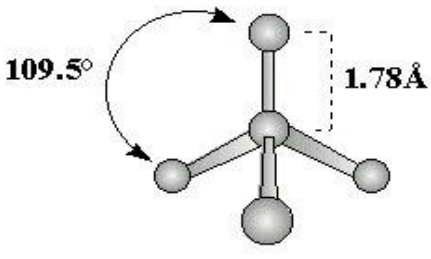
The structure of a molecule is defined by:

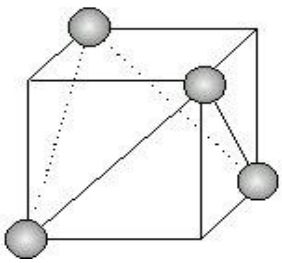
- ***The bond angles***
- ***The bond lengths***

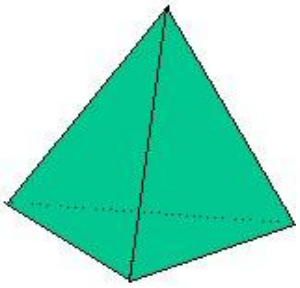
In carbon tetrachloride:

- **Each C-Cl bond length is 1.78Å**
- **Each Cl-C-Cl bond angle is 109.5°**

Carbon tetrachloride is *tetrahedral* in structure:







Molecular Geometries of AB*n* molecules

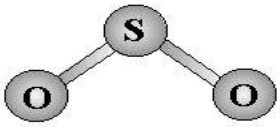
A central atom

***A* is bonded**

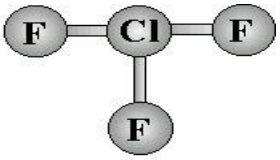
to two or more

***B* atoms**

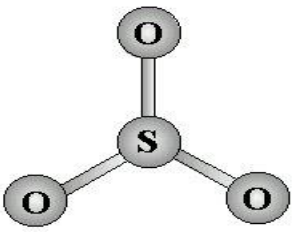
Linear



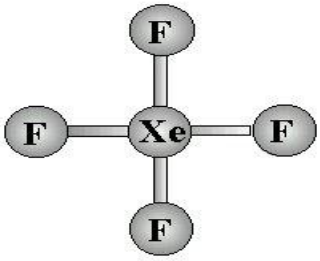
Bent



T-shaped

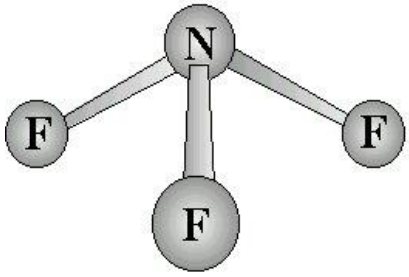


Trigonal Planar

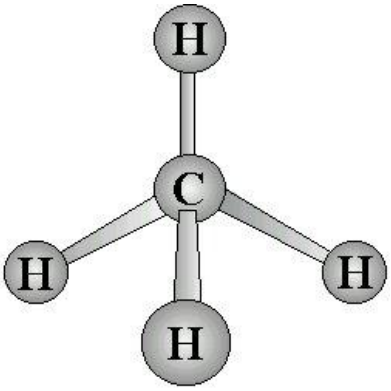


Square Planar

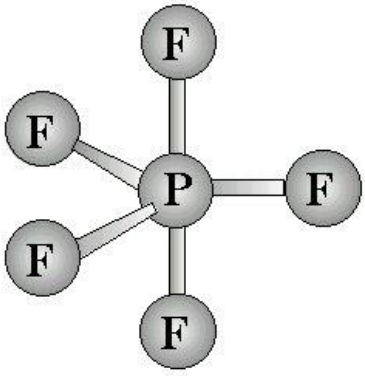
These structures can generally be predicted, when A is a nonmetal, using the "valence-shell electron-pair repulsion model (VSEPR)



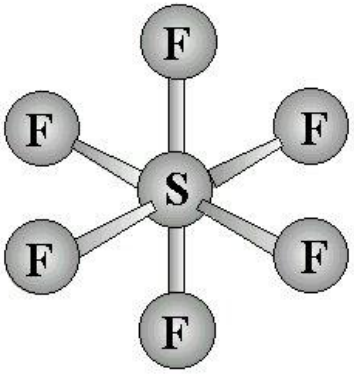
Trigonal pyramidal



Tetrahedral



Trigonal bipyramidal



Octahedral

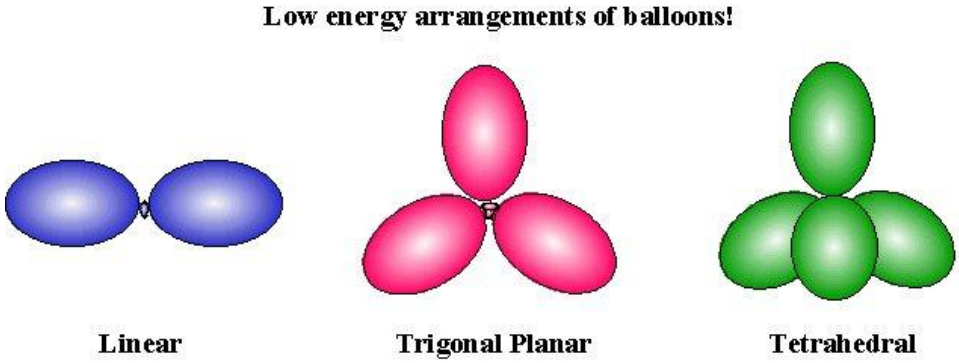
VSEPR Theory

Valence Shell Electron Pair Repulsion Theory

VSEPR Theory is one method that chemists use to predict the shapes of molecules. This theory predicts that electron pairs, whether involved in bonds or as non-bonding pairs, will adopt a geometry in which they maximize the distance from one another in order to minimize repulsions. This will result in a geometry with the lowest possible energy.

The Valence Shell Electron Pair Repulsion Model

Balloons tied together adopt arrangements which minimize steric clashes between neighbors:



- **Atoms are bonded together by electron pairs in valence orbitals**
- **Electrons are all negatively charged and tend to repel other electrons**
- **Bonding pairs of shared electrons tend to repel other bonding pairs of electrons in the valence orbital**

The best spatial arrangement of the bonding pairs of electrons in the valence orbitals is one in which the repulsions are minimized

Like the balloon example:

- **Two electron pairs in the valence orbital are arranged linearly**
- **Three electron pairs are organized in a trigonal planar arrangement**
- **Four electron pairs are organized in a tetrahedral arrangement**
- **Five electron pairs are arranged in a trigonal bipyramid**
- **Six electron pairs are organized in an octahedral arrangement**

Two Regions of Electron Density

The maximum distance two regions of electron density can get away from affords a geometry called *linear*.

The *red spheres* represent the atoms in the molecule.
The *gray ovals* represent bonding regions (a single bond , a double bond, or a triple bond - each represents one region).

linear

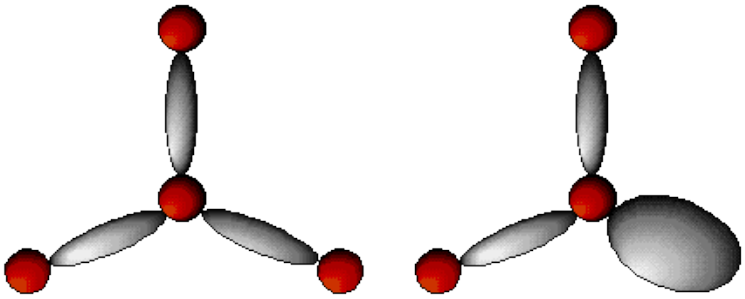
Three Regions of Electron Density

The maximum distance three regions of electron density can get away from affords a geometry called *trigonal planar*.

There are two possible *shapes* of molecules whose geometry is *trigonal planar*.

- **In the first instance, all the regions are bonding regions and the shape of the molecule is the same as the geometry around the central atom, *trigonal planar*.**
- **In the second instance, there are two bonding regions and one non-bonding region, the shape of molecules of this type is called *bent*.**

The large gray areas represent non-bonding pairs of electrons.



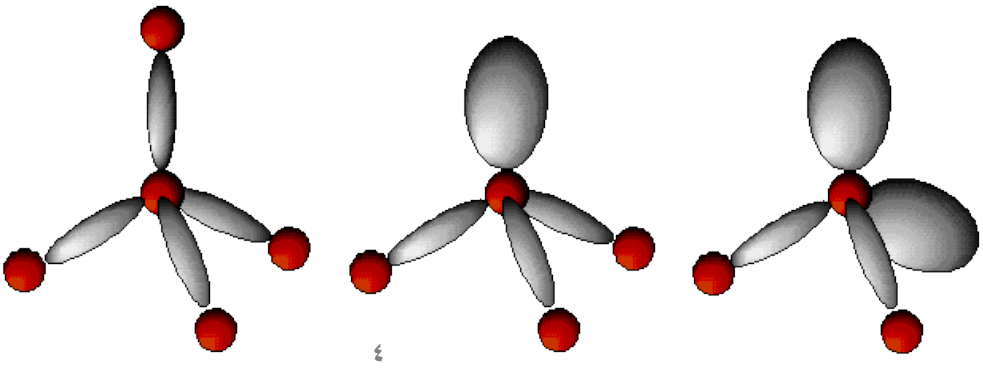
trigonal planar bent

Four Regions of Electron Density

The maximum distance four regions of electron density can get away from affords a geometry called *tetrahedral*.

There are three possible *shapes* of molecules whose geometry is *tetrahedral*.

- **In the first instance, all the regions are bonding regions and the shape of the molecule is the same as the geometry around the central atom, *tetrahedral*.**
- **In the second instance, there are three bonding regions and one non-bonding region, the shape of molecules of this type is called *trigonal pyramidal*.**
- **In the third instance, there are two bonding regions and two non-bonding regions, the shape of molecules of this type is called *bent*.**



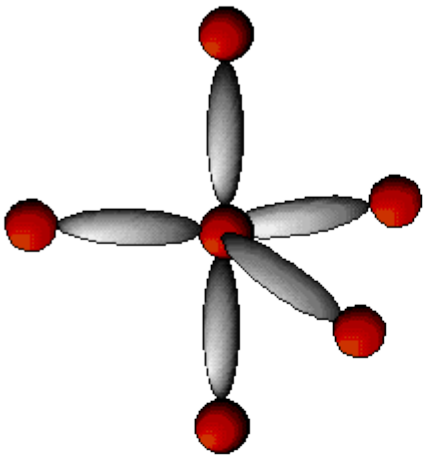
tetrahedral trigonal pyramidal bent

Five Regions of Electron Density

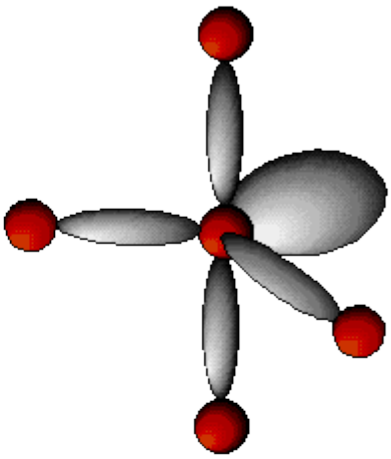
The maximum distance five regions of electron density can get away from affords a geometry called *trigonal bipyramidal*.

There are four possible *shapes* of molecules whose geometry is *trigonal bipyramidal*.

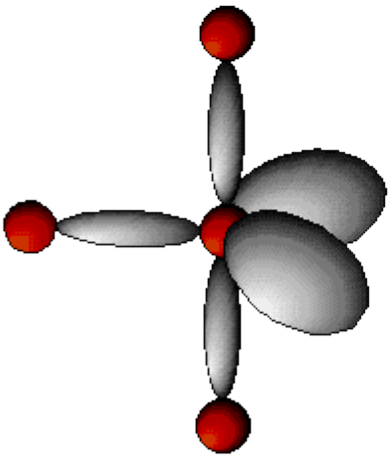
- **In the first instance, all the regions are bonding regions and the shape of the molecule is the same as the geometry around the central atom, *trigonal bipyramidal*.**
- **In the second instance, there are four bonding regions and one non-bonding region, the shape of molecules of this type is called *distorted tetrahedral*.**
- **In the third instance, there are three bonding regions and two non-bonding region, the shape of molecules of this type is called *T-shaped*.**
- **In the fourth instance, there are two bonding regions and three non-bonding regions, the shape of molecules of this type is called *linear*.**



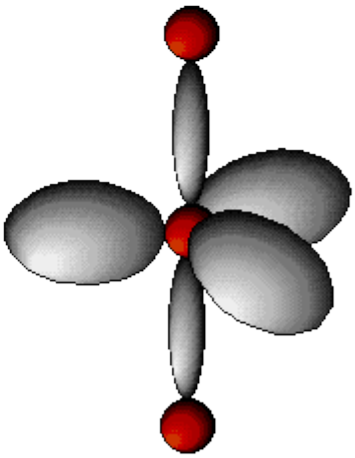
trigonal bipyramidal



distorted tetrahedral



T-shaped



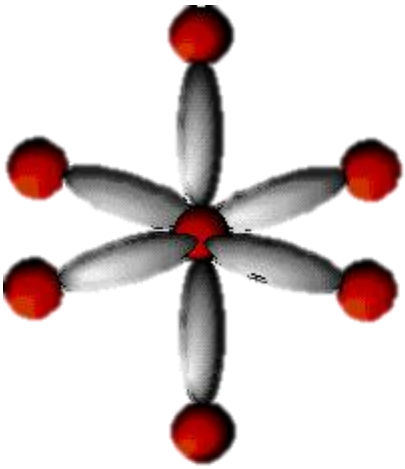
linear

Six Regions of Electron Density

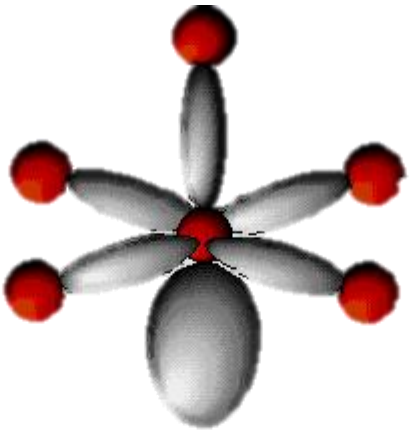
The maximum distance six regions of electron density can get away from affords a geometry called *octahedral*.

There are five possible *shapes* of molecules whose geometry is *octahedral*.

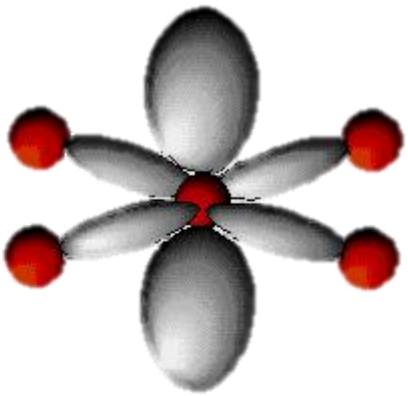
- **In the first instance, all the regions are bonding regions and the shape of the molecule is the same as the geometry around the central atom, *octahedral*.**
- **In the second instance, there are five bonding regions and one non-bonding region, the shape of molecules of this type is called *square pyramidal*.**
- **In the third instance, there are four bonding regions and two non-bonding regions, the shape of molecules of this type is called *square planar*.**
- **In the fourth instance, there are three bonding regions and three non-bonding regions, the shape of molecules of this type is called *T-shaped*.**
- **In the fifth instance, there are four bonding regions and two non-bonding regions, the shape of molecules of this type is called *linear*.**



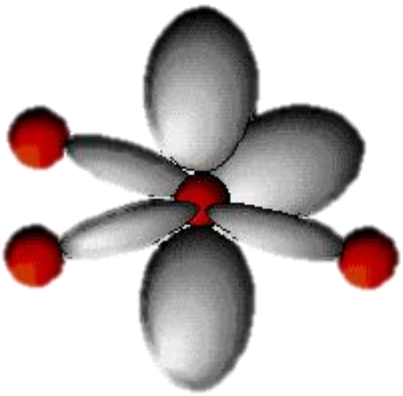
Octahedral



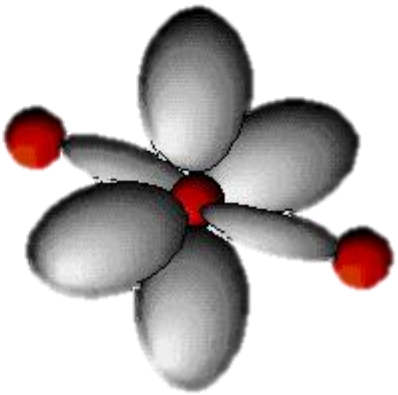
square pyramidal



square planar

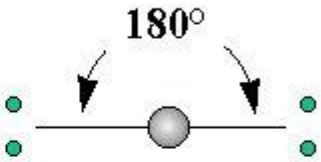
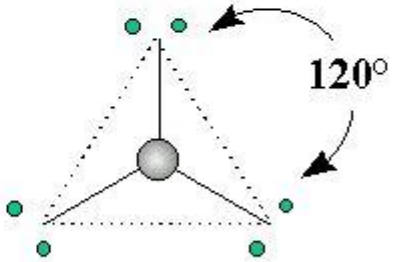
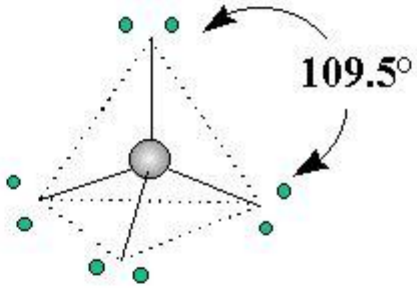
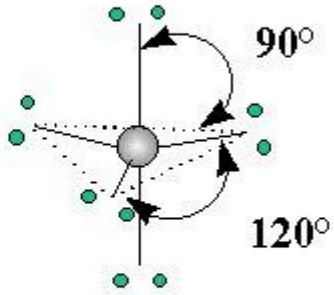
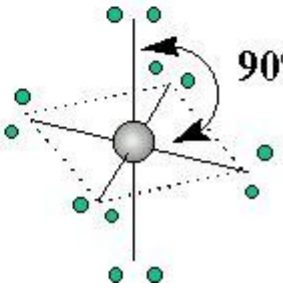


T-shaped



linear

Fig.1 The shape of a molecule can be related to these five basic arrangements .

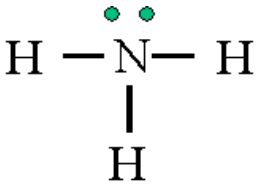
Number of electron pairs	Arrangement of electron pairs	Electron-pair geometry	Predicted bond angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramid	90° 120°
6		Octahedral	90°

Predicting Molecular Geometries

In Lewis structures there are two types of valence electron pairs:

- ***bonding pairs*** **(shared by atoms in bonds)**
- ***nonbonding pairs*** **(also called lone pairs)**

The Lewis structure of ammonia:



- **Three bonding pairs of electrons**
- **One nonbonding pair of electrons**

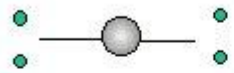
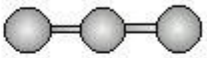
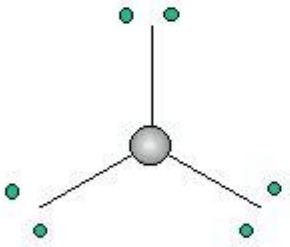
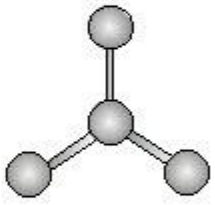
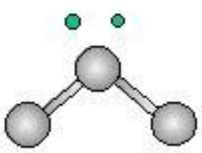
In the example (ammonia), we would predict that the three hydrogens would form the vertices of a tetrahedron, and the nonbonding electron pair the fourth. Thus, ammonia would have a *trigonal pyramide* arrangement of its H atoms .

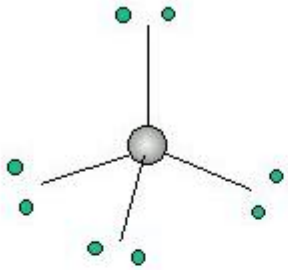
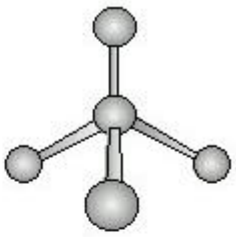
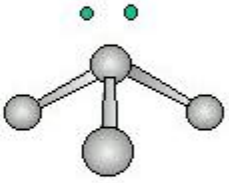
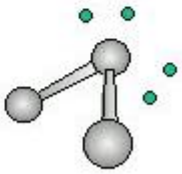
Steps involved in determining the VSEPR model:

1- **Draw the Lewis structure .**
2- **Count total number of electron pairs around the central atom .**
3- **Arrange them to minimize the electron shell repulsion .**
4- **Describe the molecular geometry in terms of the angular arrangement of the *bonding pairs* .**

Four or Fewer Valence-Shell Electron Pairs

Structural types for molecules or ions which obey the octet rule:

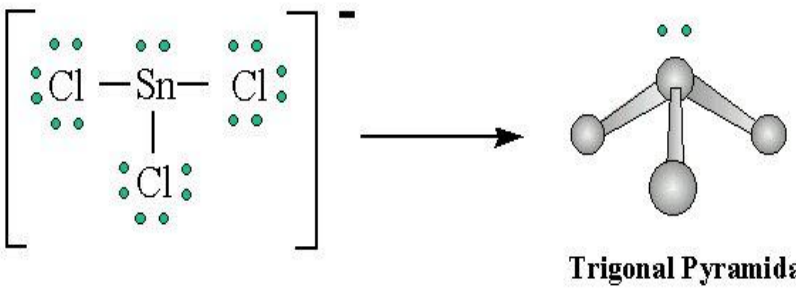
Total Electron Pairs	Electron Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Examples
2	 Linear	2	0	 Linear	$HgCl_2$ $CuCl_2^-$
3	 Trigonal planar	3	0	 Trigonal planar	BF_3 $Hgcl_3$ $SnCl_2$ NO_2^-
		2	1	 Bent	

Total Electron Pairs	Electron Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Examples
4	 Tetrahedral	4	0	 Tetrahedral	CH_4 , BF_3
		3	1	 Trigonal pyramidal	NH_3 , PF_3
		2	2	 Bent	H_2O , ICl_2^+

Note: a double or triple bond is counted as <u>one</u> bonding pair when predicting geometry

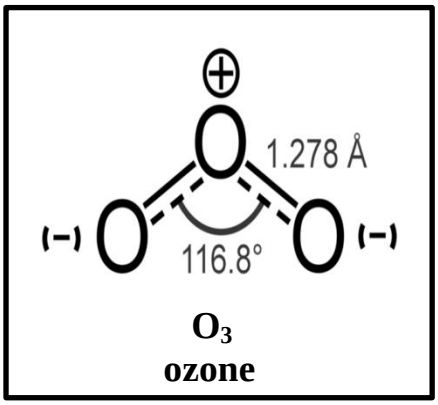
Using the VSEPR model predict the molecular geometries of

a) $SnCl_3^-$

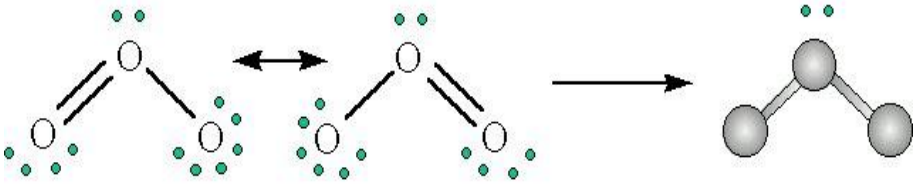


Trigonal Pyramidal

b) O_3



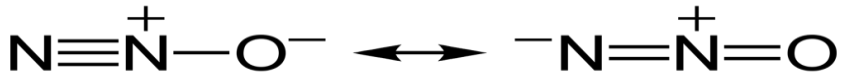
O_3
ozone



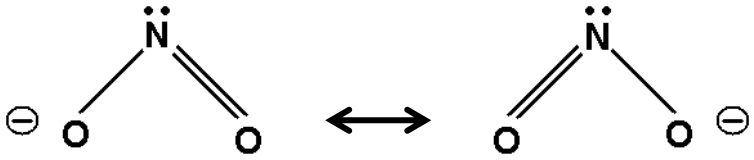
Bent

The VSEPR model can be apply to the resonance structures of Dinitrogen oxide

, N_2O , is a linear molecule .



The nitrite ion , NO_2 , has an angular structure similar to $SnCl_2$



The bond angle of NO_2 is 115° (rather than 120°) because of the effect of the nonbonding pair.

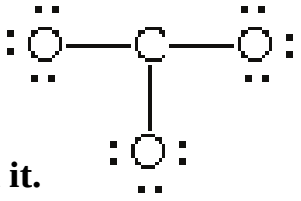
<u>Resonance Structures</u>

Sometimes, a single Lewis structure does not adequately represent the true structure of a molecule.

Consider the carbonate ion, CO_3^{2-}

carbon (C) has four valence electrons x 1 carbon = 4 e^-
oxygen (O) has six valence electrons x 3 oxygens = 18 e^-
The ion has an overall negative two charge so we add 2 e^- to give a total of 24 e^- to be placed in the Lewis structure.

Carbon is the central atom, the three oxygens are bound to it and electrons are added to fulfill the octets of the outer atoms.

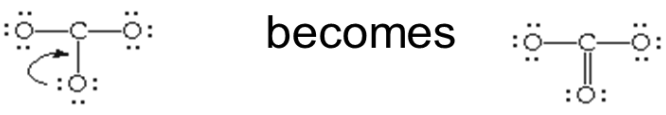


All the available electrons have been used but

carbon is electron deficient - it only has six electrons around it.

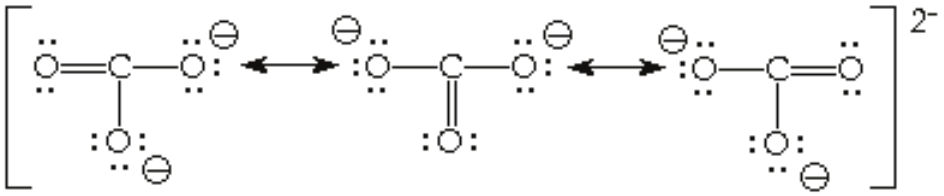
So we share a non-bonding electron pair on an oxygen with the carbon to create a double bond and thereby fulfill carbon's octet.

or

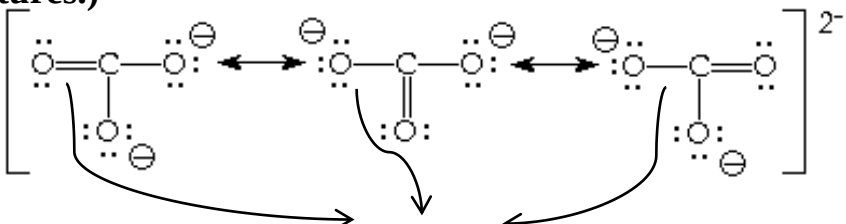


or

Three equivalent Lewis structures (formal charges are included) can be drawn for the carbonate ion.



This affords a bond order for the carbon - oxygen bond of 1 1/3. (4 bonds averaged over three structures.)

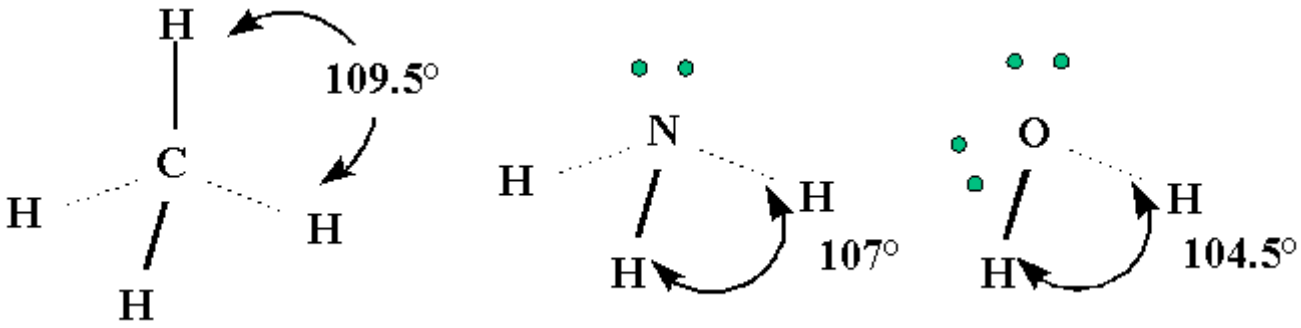


Bond Order = $\frac{2 + 1 + 1}{3 \text{ structures}}$ = 1 1/3

<u>The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles</u>

The VSEPR model can be used to explain slight distortions from ideal bond geometries observed in some structures.

Methane, ammonia and water all have tetrahedral electron-pair geometries, but the bond angles of ammonia and water are slightly distorted from an ideal tetrahedron:



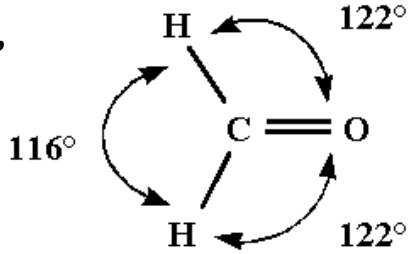
The bond angles decrease as the number of nonbonding electron pairs increases

<u>Multiple bonds:</u>

contain higher electron density than single bonds also distort geometry by crowing the bonding pairs of single bonds:

Electrons in multiple bonds, like nonbonding electrons, exert a greater repulsive force on adjacent electron pairs than do single bonds .

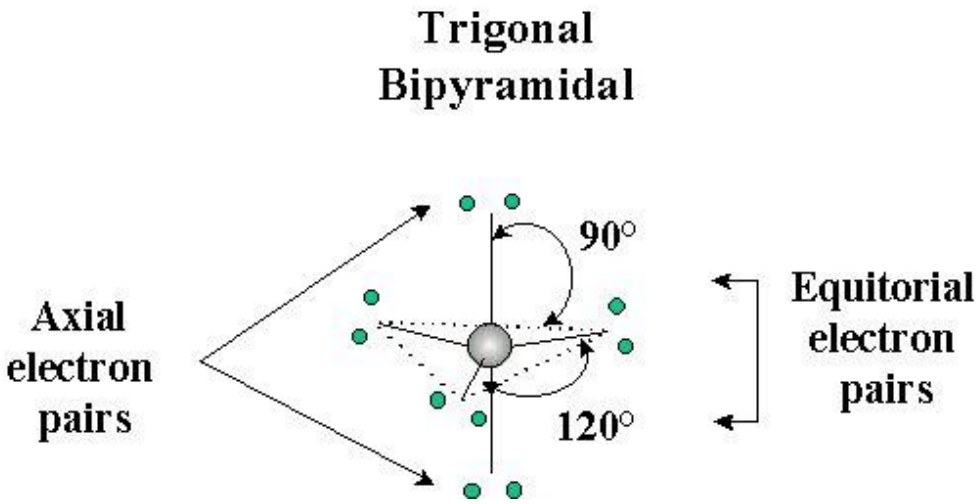
Formaldehyde



Geometries of Molecules with Expanded Valence Shells:

- **When the central atom has '*d*' orbitals available (*n* = 3 and higher) then it may have more than 4 electron pairs around it.**
- **Such atoms exhibit a variety of molecular geometries:**

The *trigonal bipyramidal* arrangement for atoms with 5 pairs of valence electrons contains two geometrically distinct types of electron pairs, *axial* and *equitorial*:



If there is a non-bonding pair of electrons (a "larger" electron cloud), it will go in the axial position to minimize electron repulsion

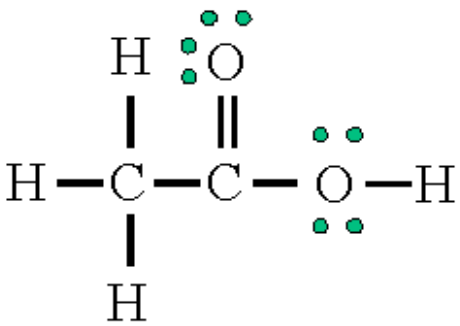
The *octahedral* structure contains 6 pairs of valence electrons. All positions are *equivalent* and at 90° from other electron pairs.

If there is one nonbonding pair of electrons, it makes no difference where we place them. *However, if there are two nonbonding pairs of electrons, the second pair will be 180° from the first to minimize steric interactions*

Molecules with no central atom:

The *VSEPR* model can be used to determine the geometry of more complex molecules

Acetic Acid



- **The first carbon has four pairs of valence electrons and will be tetrahedral**
- **The second carbon has "three" (multiple bonds count as one in VSEPR) and will be trigonal planar**
- **The oxygen on the right has four and will be tetrahedral (only two have bonds and thus it will appear as a "bent" conformation):**